L7   ANSWER 30 OF 64   CA   COPYRIGHT 2003 ACS
AN   120:163174   CA
TI   C-H Bond Activation by Metal Oxo Species: Oxidation of Cyclohexane by
       Chromyl Chloride
AU   Cook, Gerald K.; Mayer, James M.
CS   Department of Chemistry, University of Washington, Seattle, WA, 98195, USA
SO   Journal of the American Chemical Society (1994), 116(5), 1855-68
AB   Chromyl chloride (CrO2Cl2) reacts with cyclohexane solvent at 75 °C to give
       a dark ppt. along with chlorocyclohexane and a small amt. of cyclohexene
       (in 10.0 and ca. 0.3% yields based on chromium). Hydrolysis of the ppt.,
       or treatment with a coordinating org. solvent such as acetonitrile, yields
       cyclohexanone (8.0%) and chlorocyclohexanone (2.5%). Spectroscopic studies
       of the ppt. indicate that the ketone products are present intact as σ-only
       ligands. Iodometric titrns. of the complex show the av. chromium oxidn.
       state to be 3.41. The obsd. org. products account for only 26% of the
       chromium oxidizing equiv. used in the reaction; the remainder are most
       likely consumed in the formation of ring-opened products such as adipic
       acid. The three major org. products grow in concurrently during the course
       of the reaction and are not substantially oxidized further under the
       reaction conditions. Cyclohexene, however, is readily oxidized by CrO2Cl2
       to give mostly ring-opened products with some 2-chlorocyclohexanone and
       cyclohexanone. The rate of reaction of CrO2Cl2 with cyclohexane, monitored
       via the optical absorbance of the CrO2Cl2 vapor above the soln., is first
       order in chromium. Rates were reproducible with no sign of an induction
       period. Reaction in the presence of the radical trap CBrCl3 gave some
       bromocyclohexane. The data indicate that the reaction proceeds by initial
       hydrogen atom transfer from cyclohexane to CrO2Cl2. The cyclohexyl radical
       is rapidly trapped by oxidizing chromium species via one of three pathways:
       (i) chlorine atom abstraction, (ii) formation of a C-O bond, and (iii)
       transfer of a second hydrogen atom. The mass balance of the reaction and
       results from reactions of cyclohexane-d12 are consistent with this
       mechanism. The ability of CrO2Cl2 to abstr. a hydrogen atom from
       cyclohexane is remarkable, as it is a closed-shell diamagnetic species, not
       a radical. It is proposed that the hydrogen atom abstracting ability
       derives from the ability of CrO2Cl2 to make a strong O-H bond by accepting
       a hydrogen atom. The strength of the analogous O-H bond made by
       permanganate can be calcd. from a thermodn. cycle to be 80 kcal/mol. Using
       this value for CrO2Cl2 provides both a qual. and a quant. understanding of
       the hydrogen atom transfer step. The implications of this perspective for
       transition metal mediated hydrogen atom transfer reactions are discussed.

L7   ANSWER 45 OF 64   CA   COPYRIGHT 2003 ACS
AN   110:12791   CA

TI Scientific considerations for empirical determination of regional source-receptor relationships
AU Hidy, G. M.
CS Desert Res. Inst., Reno, NV, 89506, USA
SO Atmospheric Environment (1967-1989) (1988), 22(9), 1801-20
AB Investigations required to support the design of a large-scale field expt. to derive empirical relationships between source emissions and receptor conditions are discussed. The applications of the approach is on scales where long-range transport of air pollutants, particularly SOx and NOx can take place. The region studied was eastern North America. The studies examd. the exptl. concept using tracer releases to track emissions, the availability of suitable tracer technol., the availability of appropriate empirical source-receptor models, the uncertainties and natural variability influencing the expt., and a formal framework to construct a suitable measurement and interpretative design. An expt. can be devised that uses a combination of inert and chem. reactive tracers to establish source-receptor relations, and simulates atm. behavior of SO2 and NOx. **Isotopic** S and N **tracers** are available as well as inert tracers of perfluorocarbons rarely found in the atm. Two empirical model concepts are available, one using a statistical regression format and the other a differential **mass balance**. Based on theor. calcns. and available measurements uncertainties induced with measurements and atm. fluctuations are estd. to be large, making the projected exptl. results uncertain at the outset. A statistical design structure using objective anal. can be specified from meteorol. experience to improve the capability of dealing with the uncertainties. The results of the studies are discussed to provide a foundation for design of a massive aerometric tracer expt. (MATEX).

L7 ANSWER 52 OF 64 CA COPYRIGHT 2003 ACS
AN 106:216709 CA
TI Use of stable sulfur isotopes to monitor directly the behavior of sulfur in coal during thermal desulfurization
AU Liu, C. L.; Hackley, K. C.; Coleman, D. D.
CS Illinois State Geol. Surv., Champaign, IL, 61820, USA
SO Fuel (1987), 66(5), 683-7
AB A method was developed by using stable S isotope analyses to monitor the behavior of S forms in a coal during thermal desulfurization. In this method, the natural stable isotopic compn. of the pyritic and org. S in coal is used as a tracer to follow their mobility during the desulfurization process. This tracer method is based on the fact that the isotopic compns. of pyritic and org. S are significantly different in some coals. Isotopic results of pyrolysis expts. at 350-750° indicate that the S released with the volatiles is predominantly org. S. The pyritic S is evolved in significant quantities only when pyrolysis temps. are >500°. The presence of pyrite has no effect on the amt. of org. S evolved during pyrolysis. The chem. and isotopic **mass balances** achieved from 3 different samples of the Herrin (No. 6) coal of the Illinois Basin demonstrate that this stable **isotope tracer** method is quant. The main disadvantage of this tracing technique is that not all coals contain isotopically distinct org. and pyritic S.

L7 ANSWER 60 OF 64 CA COPYRIGHT 2003 ACS
AN 93:83040 CA
TI On-line data evaluation used in automatic mass spectrometric **isotope dilution** analysis of nuclear fuels
AU Koch, Lothar; Brandalise, Bruno
CS Jt. Res. Cent., Karlsruhe Establ. Eur. Inst. Transuranium Elem., Karlsruhe, D-7500, Fed. Rep. Ger.

AB   Automatic on-line data evaluation was used for isotope anal. of nuclear
      fuels. Various automates, (**balance**, α- and **mass**-spectrometers), are linked
      via special interfaces and 3 minicomputers to an IBM 370. The system
      described speeds up the analyses and guarantees the confidentiality and
      data security required for nuclear materials safeguards.

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STN INTERNATIONAL LOGOFF AT 07:41:02 ON 19 JUN 2003

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      (FILE 'HOME' ENTERED AT 08:20:20 ON 19 JUN 2003)
      FILE 'CA' ENTERED AT 08:20:29 ON 19 JUN 2003
L1 142409 S (SPECIE OR ION OR ANION OR CATION OR CHROMIUM OR NICKEL)(8A)(CONVER?
            OR INTERCONVER? OR CROSSOVER OR CROSS OVER OR REDOX OR REDUCTION OR
            REDUCING OR OXIDAT? OR OXIDIZ?)
L2   16826 S L1(6A)(DETECT? OR MONITOR? OR MEASUR? OR DETERMIN? OR FOLLOW? OR
            ASSAY? OR ANALY? OR ASSES? OR ESTIMAT? OR EVALUAT? OR INVESTIGAT? OR
            EXAMIN? OR STUDY? OR STUDIE#)
L3   346 S L2 AND ISOTOP?
L4   12 S L2 AND ISOTOP?(2A)(2 OR 3 OR 4 OR TWO OR THREE OR FOUR OR DOUBLE OR
            TRIPLE OR MULTI OR MULTIPLE OR MULTIISOTOP? OR PLURAL?)
L5   44 S L3 AND (SPIKE OR ADDITION)
L6   37 S L3 AND(CHROMIUM OR 50CR? OR 53CR? OR CR III OR CR VI OR CR###(2A)
            STATE)
L7   80 S L4-6
L8   52 S L7 NOT PY>1997
L9   28 S L7 NOT L8
L10   9 S L9 AND(DILUT? OR CHROMATOG?)
L11 17173 S (SPECIE OR ION OR ANION OR CATION OR CHROMIUM OR
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L12   2930 S L11(6A)(DETECT? OR MONITOR? OR MEASUR? OR DETERMIN? OR FOLLOW? OR
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            EXAMIN? OR STUDY? OR STUDIE#)
L13   2864 S L12 NOT L2
L14   153 S L13 AND ISOTOP?
L15   11 S L13 AND ISOTOP?(2A)(2 OR 3 OR 4 OR TWO OR THREE OR FOUR OR DOUBLE OR
            TRIPLE OR MULTI OR MULTIPLE OR MULTIISOTOP? OR PLURAL?)
L16   13 S L14 AND (SPIKE OR ADDITION)
L17   10 S L14 AND(CHROMIUM OR 50CR? OR 53CR? OR CR III OR CR VI OR CR###(2A)
            STATE)
L18   18 S L15-17 NOT PY>1997
L19   14 S L15-17 NOT L18
L20   2 S L19 AND DILUT?
L21   81 S L8,L10,L18,L20

=> d bib,ab 1-81

L21   ANSWER 62 OF 81 CA COPYRIGHT 2003 ACS
AN   101:3352 CA
TI   A least-squares approach to the quantitation of stable isotopes in mass
      spectrometry
AU   Lee, Wai Nang Paul; Whiting, James S.; Fymat, Alain L.; Boettger, Heinz G.
CS   Dep. Pediatr., Univ. California, Los Angeles, CA, 90024, USA
SO   Biomedical Mass Spectrometry (1983), 10(12), 641-5
AB   A least-squares method was adapted for the quantitation of stable isotopes
      in mass spectrometry. The method uses the normalized spectra of the **2**

isotope species and the obsd. intensities to calc. the isotope ratio by a series of matrix manipulations and is applicable to systems with multiple overlapping ions. The method is used to establish the expected sensitivity of measurement of 15N enrichment of an amino acid by a focal plane mass spectrometer equipped with an electrooptical ion detector. Since multiple spectral peaks are used, the relation between addnl. spectral information and the redn. in variance in ion-current statistics can be demonstrated. The example suggests a method for optimization of simultaneous ion monitoring or limited scanning methods by **monitoring** the no. of **ions** which would contribute to the **redn**. of variance of the ion current of the compd. of interest.

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STN INTERNATIONAL LOGOFF AT 08:51:17 ON 19 JUN 2003